



Application Note 124

A Visual Method for the Detection of Arsenic 0–500 µg/L Dan Kroll, Hach Company, Loveland Colorado

Introduction

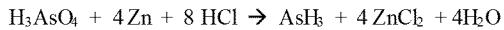
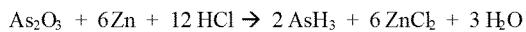
Arsenic, a common contaminant of ground water, has been found to adversely affect human health at levels as low as 10 µg/L. The current USEPA maximum contaminant level (MCL) for arsenic is 50 µg/L, but may be revised to between 5 and 20 µg/L shortly. The current World Health Organization (WHO) recommended MCL for arsenic in drinking water is 10 µg/L.

The quantification of trace amounts of arsenic in water samples has always been a problem. Current methods rely on expensive apparatus, complicated procedures, and dangerous chemical reagents. Low cost test kits, available in the past, had a working range of 100 to 3000 µg/L, which is not sensitive enough to monitor drinking water supplies. The new Hach Arsenic Kit addresses many of these problems.

Summary of the New Method

In the Hach method*, hydrogen sulfide is first oxidized to sulfate to prevent interference, then the oxidizing environment is neutralized. Next, sulfamic acid and powdered zinc react to create strong reducing conditions in which inorganic arsenic is reduced to arsine gas. The arsine gas then reacts with mercuric bromide, impregnated onto a test paper to form mixed arsenic/mercury halogenides (e.g. AsH₂HgBr). The mixed halogenides discolor the test strip to a degree proportional to the concentration of arsenic in the sample. The color change is from white to yellow to tan to brown.

Reducing Chemical Hazards



As the reactions above indicate, arsine gas (AsH₃) is commonly generated by reduction with

zinc metal and hydrochloric acid. The Hach method substitutes a safer, more easily transported, solid acid (sulfamic acid, packaged as a granular powder) for the hydrochloric acid used in most kits. The zinc powder and the reagents in the Hach method are packaged in convenient unit doses to minimize handling. The design and packaging of the mercuric bromide strip eliminates the need for contact with the mercuric bromide.

Arsine gas is toxic. By containing the gas and focusing it on a very small surface, Hach's unique reaction vessel cap minimizes arsine exposure and increases test sensitivity. A 0.5 x 0.5-inch mercuric-bromide-coated reaction pad is exposed to the gas through a hole only 3/16 inch in diameter. This arrangement allows all of the generated gas to come into contact with the mercuric bromide and be reacted. The excess paper around the hole provides sufficient reactant to absorb the excess generated arsine.

Reaction Vessel with Cap and Strip



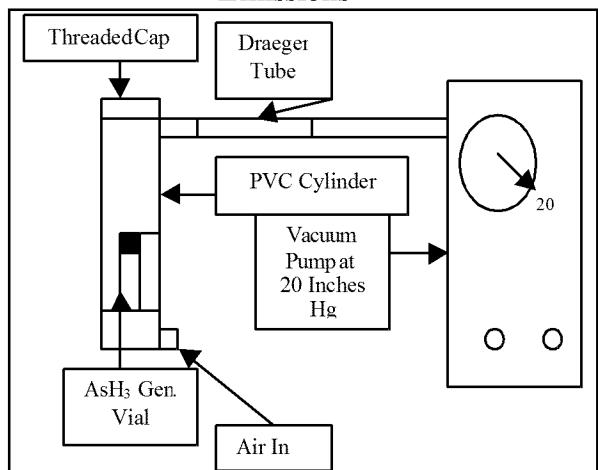
Test strip exposed to 500 µg/L arsenic



* Patent pending

The following experiment verifies that arsine exposure is in fact minimized. The Hach apparatus was compared to a currently available test kit using the system shown below.

System for Checking Arsine Emissions



The Draeger-TubeTM¹ detects arsine gas in air. The distance that a purple color travels up the tube quantifies the amount of arsine present. Samples containing 500 µg/L arsenic were tested using both methods. The Hach method uses a 50 mL sample and the competitor uses a 5 mL sample. The vacuum pump was set at 20 inches of Hg and allowed to run continually for the full 30 minutes of each test. The results of the experiment are shown here.

Results of Arsine Exposure Test

Apparatus	mg/L AsH ₃ after 30 min.
Competitor with no test strip	0.8 ppm
Competitor with test strip	0.3 ppm
Hach with no test strip	> 3.0 ppm
Hach with test strip	0.0 ppm

Even though it generates more arsine gas overall, the new Hach apparatus minimizes the release of arsine gas to the atmosphere, where it might pose a hazard.

Improved Sensitivity

The larger sample size, combined with the unique design of the cap for Hach's reaction vessel, focuses the arsine gas on a very small surface. The generated arsine must react with the test strip before it can exit the reaction vessel. This allows for a calibrated range of 0 to 500 µg/L (ppb). The calibration scale has distinct steps at 0, 10, 30, 50, 70, 300, and 500 µg/L.

Sulfide Interference

Unfortunately, during the reduction of arsenic to arsine gas, sulfides are also reduced to form hydrogen sulfide (H₂S). Hydrogen sulfide reacts with the mercuric bromide test paper in the same way as the arsine gas, causing an interference. Current methods for removing sulfide interference entail passing the arsine gas stream through a scrubber to remove the hydrogen sulfide. These scrubbers are usually made of cotton that has been soaked in lead acetate solution (zinc and copper have also been used but have been found to be less efficient). The sulfide reacts with the lead on the cotton to form solid lead sulfide, thereby removing it from the arsine gas stream.

There are some drawbacks to this method. First, the seal must be tight enough to obligate the passage of all of the gas through the scrubber. Then the rate of gas evolution must be controlled to allow adequate contact time for all of the sulfide to react. Lastly, the operator must handle and dispose of hazardous lead acetate and lead sulfide.

Hach's new method eliminates the need to rely on lead acetate to remove sulfide interference. The Hach method employs the addition of three unit-dose reagent pillows to convert the sulfide present in the sample to a form that will not interfere in the test.

First, sodium phosphate dibasic and potassium monopersulfate (Oxone®²) are added to the sample. This results in the formation of strong oxidizing conditions. Sulfides are oxidized to sulfate in which form they no longer interfere. Next, a mixture of disodium and tetrasodium EDTA is added to the sample to remove any residual Oxone® and to prevent its interference in

¹ Draeger-Tube™ is a trademark of Draegerwerk AG

² Oxone® is a registered trademark of DuPont

the subsequent reduction and evolution of arsine gas.

Tests were run to determine the levels at which sulfide interfered. A sulfide concentration was said to interfere if the color developed in the arsenic test exceeded more than $\frac{1}{2}$ of the step between 0 and 10 $\mu\text{g/L}$ arsenic on the color chart, or approximately 5 $\mu\text{g/L}$ arsenic.

Sodium sulfide standards were prepared and their concentrations were verified using method # 8131 (Methylene Blue), the Hach DR-4000 Spectrophotometer, and the instrument-stored program for sulfide. When using the kit reagents, it was found that as much as 5 mg/L S^{2-} could be tolerated before the acceptance criterion of 5 $\mu\text{g/L}$ arsenic equivalence was exceeded.

Interferences

Various substances likely to interfere with the method were evaluated using the same acceptance criterion (5 $\mu\text{g/L As}$).

The following were found to interfere at concentrations greater than those listed.

Ion or Substance	Concentration
Sulfide (S^{2-})	5 mg/L
Selenium (Se)	1 mg/L
Antimony (Sb)	0.25 mg/L
Tellurium (Te)	Likely to interfere, but not tested

The following did not interfere at the levels tested.

Ion or Substance	Level Tested
Hardness	1000 mg/L CaCO_3
Alkalinity	1000 mg/L CaCO_3
Iron (Fe)	10 mg/L
Temperature	10 to 40 degrees C

Organic Arsenic

Organic arsenic represents a small proportion of the arsenic found in most systems. However, in some cases where anthropogenic sources of arsenic, such as pesticides, are a factor, it can contribute significantly to the total arsenic present. Most tests must include complicated digestions and other manipulations to detect organic arsenic compounds. This method is designed to detect inorganic arsenic. To quantify

total arsenic, including organic arsenic, with this method, modify the procedure as follows:

Collect the sample in a glass beaker. Add the disodium phosphate and Oxone®. Place the beaker in a boiling water bath for 30 minutes. Remove the beaker from the water bath and transfer the contents to the reaction vessel. Allow the sample to cool to room temperature. Complete the procedure as for inorganic arsenic.

Results for Various Organic Arsenics

Compound	500 $\mu\text{g/L Std}$	10 $\mu\text{g/L Std}$
Cacodylic acid (Dimethyl arsenic acid) $\text{C}_2\text{H}_8\text{AsO}_2\text{Na}$	500	10
o-Arsanilic acid $\text{H}_2\text{NC}_6\text{H}_4\text{AsO}_3\text{H}_2$	500	10
p-Arsanilic acid $\text{H}_2\text{NC}_6\text{H}_4\text{AsO}_3\text{H}_2$	500	10
Arsenazo III $\text{C}_{22}\text{H}_{18}\text{N}_4\text{O}_{14}\text{S}_2\text{A}$ S_2	500	10

The results on all organic arsenics tested showed 100% recovery at both 10 and 500 $\mu\text{g/L As}$.

Testing Samples of Bottled Water

Samples of bottled water from a variety of sources were tested, and then spiked and retested. The samples showed an initial arsenic level that closely matched levels by the Natural Resource Defense Council (NRDC) reported for these products.

Bottled Water Results			
Source	Initial Detected ($\mu\text{g/L}$)	With 10 $\mu\text{g/L Spike}$	NRDC Reported Value
Michigan	0	10	Not Done
France	0	10	0
Italy	≈ 4	Slightly >10	5
Utah	0	10	0
California	10	>10	11,12,17
Fiji Islands	≈ 4	Slightly >10	Not Done
Montana	0	10	0

Various samples of well and tap water from Iowa and Colorado, some of which contained large amounts of iron and organic material, were spiked and tested.

Well and Tap Water Results

Source	Initial Detected ($\mu\text{g/L}$)	With 10 $\mu\text{g/L}$ Spike
Well near Madrid, Iowa	Slightly < 10	> 10
Well near Ames, Iowa	0	10
Well near Kelley, Iowa	0	10
Ames, Iowa tap	0	10
Loveland, CO tap	0	10
Ft. Collins, CO tap	0	10

Conclusion

The method described offers a safe, easy, and accurate method for determining trace arsenic levels inexpensively, and it is versatile enough to detect total arsenic including organic compounds.



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